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Special Issue Reprint

Block Copolymers with Crystallizable Blocks: Synthesis, Self-Assembly and Applications

Edited by: Holger Schmalz and Volker Abetz

Block copolymers with crystallizable blocks have moved into the focus of current research, owing to their unique self-assembly behaviour and properties. New synthetic concepts give, for example, even access to tetrablock copolymers with four crystalline blocks, bio-based thermoplastic elastomers (e.g., based on ABA triblock copolymers with poly(*L*-lactide) (PLLA) hard segments), and allow new, exciting insights into the interplay of microphase separation and crystallization in controlling self-assembly in bulk (confined *vs.* break-out crystallization). Concerning self-assembly in solution, crystallization-driven self-assembly (CDSA) paved the way to a myriad of crystalline-core micellar structures and hierarchical superstructures that were not accessible before via self-assembly of fully amorphous block copolymers. This allows for the production of cylindrical micelles with defined lengths, length distribution, and corona chemistries (block type or patchy corona), as well as branched micelles and fascinating micellar superstructures (e.g., 2D lenticular platelets, scarf-shaped micelles, multidimensional micellar assemblies, and cross and “windmill”-like supermicelles). This Special Issue brings together new developments in the synthesis and self-assembly of block copolymers with crystallizable blocks and also addresses emerging applications for these exciting materials. It includes two reviews on CDSA and eight contributions spanning from membranes for gas separation to self-assembly in bulk and solution.

